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Mercury

Levels in Lake Huron Sediment

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Environment Ontario

MERCURY LEVELS IN
LAKE HURON SEDIMENT

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SUMMARY

1. Mercury levels in sediment samples from seven sampling points in Lower Lake Huron were determined by various analytical techniques in the Ministry of the Environment laboratory. Data ranged from a low of 9.1 ppb to a high of 39 ppb, with an average of approximately 20 ppb.
2. The results obtained were in the same range as data previously reported by O.W.R.C. on sediments from Lower Lake Huron. The average of previous data was approximately 20 ppb.
3. A modification of the Environmental Protection Agency's water method appears to be suitable as a check method for sediment analyses, but the method of choice for samples containing mercury in the 1 to 100 ppb range is the pyrolysis technique.



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INTRODUCTION.

The mercury content of the sediments in Lake Huron is of considerable significance because of its importance with respect to establishing background mercury levels in the St. Clair system* sediments. In 1970, Ontario Water Resources Commission (now Ministry of the Environment, within which O.W.R.C. merged) sampled and analyzed sediments from stations in Southern Lake Huron near the mouth of the St. Clair River, and obtained the following data:

<u>Lab. No.</u>	<u>Station No.</u>	<u>Hg ppm.</u>	<u>ppb.</u>
M18-55	38	0.00	0
M18-56	40	0.03	30
M18-57	43	0.03	30
M18-58	45	0.01	10

This data agrees quite well with analyses of surface soils taken from the same general area and reported by Klein (1). Klein reported an average of around 0.03 ppm in samples taken from soils distant or windward from the St. Clair River-Lake St. Clair area, and states "the value 0.03 ppm may represent the natural concentration in these soils". Other workers have reported values for soils in Sweden as being between 0.020 and 0.920 ppm (20 and 920 ppb) (2) and in England (natural mercury content) as 0.01 to 0.06 ppm (10 to 60 ppb) (3).

Work by Jonasson and Boyle, of the Geological Survey of Canada (4), indicates that the normal mercury content of stream and river sediments, and of lake sediments, is from 0.010 to 0.70 ppm with a mean of 0.073 ppm. The content for normal soils is stated as .020-.150 ppm, with a mean of 0.07 ppm, and tills, glacial clays, sand, etc., have a mean of 0.05 ppm.

Early Data.

The data reported in the literature tends to support the order of magnitude of mercury content the M.O.E. laboratory found

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*The St. Clair system includes the St. Clair River and Lake St. Clair.

in southern Lake Huron. However, in January 1972, data was obtained from the Canada Center for Inland Waters regarding approximately 200 sediments from Lake Huron whose values ranged from 0.054 to 0.68 ppm.

Because there was such a discrepancy between results from O.W.R.C. and Canada Center for Inland Waters, and because of the importance of this background data in Lake Huron, two of the previous O.W.R.C. samples were selected for repeat analyses by both O.W.R.C. and by Canada Center for Inland Waters. Canada Center for Inland Waters does not perform its own mercury analyses in sediments, but prepares the samples and contracts the analyses to Barringer Research in Rexdale, Ontario.

The usual preparation done by Canada Center for Inland Waters is to freeze-dry the sample, screen it to pass 20 mesh (each particle passing the screen would be 0.85 mm or smaller), then grind to pass 100 mesh (0.15 mm). Barringer Research then chemically prepare and analyze this screened, ground sample.

In the Ministry of the Environment laboratory, the usual procedure for sediment analysis is to homogenize the non-dried sample with a glass rod, and manually remove portions of the homogenate, excluding sticks, large stones (exceeding 2 mm diameter), leaves, etc. Duplicate portions of each sample are prepared using the standard wet digestion with oxidizing acids (7). At the same time a portion of sample is weighed into a beaker and dried, then reweighed. This moisture loss data is employed to convert the wet sediment values into parts per billion on a dry weight basis. The dried sample is not used for the mercury determination because of possible volatilization during drying.

The data obtained by Barringer Research and Ministry of the Environment on the two samples selected for repeat analyses was reported earlier (5, 6) and can be summarized as follows: the Ministry of the Environment laboratory, using the standard oxidizing digestion, reported 11.9 ± 2.0 ppb on sample A and 6.7 ± 2.7 ppb on sample B. The large deviation value indicates heterogeneity in both samples, but the reported levels are well within expected limits.

Barringer Research, analyzing freeze-dried, screened and ground samples of A and B, reported 21.3 ± 1.3 ppb and 16.3 ± 0.8 ppb respectively. These same screened, ground samples were

analyzed by Ministry of the Environment, who obtained 21.2 ± 0.3 ppb and 14.0 ± 0.3 ppb on A and B respectively. As a final check, the screened, ground samples were analyzed by the Ministry of the Environment laboratory, using an entirely different technique (pyrolysis) which yielded 18.7 ppb on A and 17.6 ppb on B.

These results indicate two things: screening large particles out of the sediments will tend to concentrate the mercury in the remaining fines, resulting in high mercury values being reported, and secondly, improved precision can be obtained on screened, ground and sieved sediments. These are hardly surprising conclusions, since it is known that mercury is absorbed to the surface of sediment particles. Oliver and Kinrade have stated: "Particle size is important because a fine sediment will have a larger surface area and thus should have an absorption capacity higher than that of coarse samples... considerably more metal is present in the finer samples" (8).

It appears likely that a higher relative concentration is associated with the fines remaining after screening and that removal of coarser particles would positively bias the data. The significant aspect of the experiment was that when both laboratories analyzed samples that had been prepared in an identical manner, they obtained data in the same order as previously found by O.W.R.C., that is, approximately 10 to 20 ppb.

EARLIER INTERCALIBRATION STUDIES.

Early in 1970 a series of round-robin sediment samples were distributed by the O.W.R.C. to Barringer Research Ltd., Fisheries Research Board in Winnipeg, Atomic Energy Canada Ltd., A. Jernelov in Sweden, and Chemical Projects Ltd., Toronto. The following data was reported (9).

TABLE I.

ROUND ROBIN STUDY

Laboratory	Method	Sediment 1	Sediment 2	Sediment 3
M.O.E. Rexdale,	FAAS	0.59	2.15	105.
F.R.B. Winnipeg,	FAAS	0.65	1.88	94.6
Chalk River, AEC,	NAA	0.10	0.07	11.4
Barringer Research,	FAAS	1.0	0.003	10.
Jernelov, Sweden,	FAAS	0.58	4.3	109.
Chemical Proj. Ltd.	FAAS	-	2.0	81.
Mean		0.58	1.73	68.5
Std. Dev.		0.32	1.59	45.8
n		5	6	6
R.S.D.		55%	92%	69%

The results show that A.E.C. (Atomic Energy Canada) and Barringer Research both tended to report low data for the samples containing parts per million, and higher, levels of mercury, but for samples low in mercury (less than 1 ppm) Barringer Research's data is high.

A round-robin on United States Geological Survey rock standards, distributed to several laboratories including Barringer Research and reported by Anderson and Henriques, showed that Barringer's results were higher in 5 out of 6 samples (12). These United States Geological Survey standard rocks contained mercury at levels ranging from 5 to 50 ppb. Barringer Research's data showed the greatest deviation (high by 50% or more) on the four lowest standards.

While such round robins are by no means a fool-proof method for evaluating a laboratory's accuracy, they do offer a guideline to the performance of the various laboratories in relation to one another. The indication from the results in Table I and in the Swedish report (12) is that Barringer Research was experiencing problems in sediment analyses at the time of these round-robins.

Later round-robins were participated in by the Ministry of the Environment laboratory. One such comparison involved the previously mentioned freeze-dried, screened samples of Lake Huron sediment, in which Barringer Research and the Ministry of the Environment obtained results which were in almost exact agreement. The Ministry of the Environment laboratory has taken part in at least one round-robin inter-laboratory comparison per month involving mercury, for the past three years. In cases involving sediment analysis, the data from the Ministry of the Environment laboratory has been among the closest to the mean value, indicating good accuracy and freedom from gross systematic or random errors.

The early round-robins and intercalibration studies on Lake Huron sediments appeared to indicate biased sample preparation on the part of Canada Center for Inland Waters, and possible analytical problems on the part of Barringer Research. Additional work was performed in order to corroborate the earlier data and to help define the level of mercury in sediments from southern Lake Huron. The following is a summary of our findings on the second series of Lake Huron sediment samples.

Experimental.

1. The samples arrived on August 23rd 1972 and were assigned sediment numbers X32-30 to X32-36. Each sample had been collected in three separate jars, to ensure that the laboratory was provided with adequate sample.
2. The excess water was carefully decanted from each sample, and large pebbles (diameter exceeding 10 mm) were removed and discarded. The samples were thoroughly homogenized on a Sorval Ominimixer for 20 minutes.
3. Moisture content was determined on each sample by taking an aliquot from one jar for each sample and measuring its moisture loss after air drying at ambient temperatures for at least 36 hours.

4. Duplicate aliquots were taken from the same bottles as in the above step and analyzed for mercury by the O.W.R.C. sulfuric-permanganate-FAAS procedure using the Hilger-Watts Atomspek (7).
5. The same jar for each sample was sampled again; this time the aliquot was analyzed for mercury content by the pyrolysis method (10).
6. Composite samples were prepared for each station by thoroughly mixing equal portions from each set of three jars. Moisture loss was determined on each of these composite samples.
7. Aliquots from each composite sample were analyzed for total mercury content by pyrolysis.
8. Aliquots from each composite sample were analyzed using a modification of the E.P.A. water method developed by Kopp (11) using sulfuric acid-nitric acid and potassium persulfate, digested at 90°C in a water bath, and analyzed for mercury with an L.D.C. (Laboratory Data Control) mercury meter. This data is reported as "ox.dig'n. water bath".
9. Aliquots from each composite sample were analyzed by a hot plate digestion procedure employing sulfuric-nitric acids and potassium persulfate, followed by reduction and analysis on the L.D.C. meter. This data is reported as "ox.dig'n. hot plate".
10. The dried portions of the composite samples remaining after the moisture determination (step 6) were analyzed by pyrolysis.

Experimental Results.

All results except moisture losses in the tables are expressed in ppb of mercury, reported on a dry weight basis. Each figure reported is the mean of replicate analyses, the number of replicates being:

- Pyrolysis - Single jar data; based on 2 results per sample;
- Pyrolysis - Composite data: based on 5 to 10 results per sample;
- Pyrolysis - Dried composites: based on 2 results on 4 samples.
- Ox. dign. water bath: based on 4 results per sample.
- Ox. dign. hot plate: based on 2 to 4 results per sample.

TABLE II.

MERCURY IN LAKE HURON SEDIMENTS BY
VARIOUS METHODS.

Sample Number	Moisture Content	OWRC FAAS Digestion	Pyrolysis Single Jar	Pyrolysis Composite	Pyrolysis Dried Comp	Oxid'd Dig Water Bath	Oxid'n Dig Hot Plate
X32-30	7% s 17% c	<50*	16.8±30%	13.2±24%	22	8.5	14.2
X32-31	13% s 22% c	<50*	26.0±5%	24.7±17%	23	11.5	21.7
X32-32	16% s 20% c	<50*	24.0±10%	17.4±15%	-	7.6	12.5
X32-33	17% s 25% c	<50*	9.1±3%	10.1±15%	-	8.7	11.3
X32-34	33% s 18% c	<50*	22.0±6%	22.9±10%	-	16.9	22.8
X32-35	33% s 36% c	<50*	39.0±10%	36.4±10%	27	22.3	32.4
X32-36	69% s 60% c	<50*	17.4±5%	20.4±8%	25	21.0	23.6
Mean			22	17			20

*50 ppb is the limit of detection for this technique,
for the amount of sample taken.

s : single jar,
c : composite.

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Data from Table II can be summarized to provide averages of the three most consistent methods, in Table III. This data as well as the data from the original four Lake Huron sediments analyzed in 1970 can be seen in Fig.1.

TABLE III.

MERCURY IN LAKE HURON SEDIMENT,
AVERAGE DATA:

Sample No.	Sampling Site (Lake Huron).	Hg in ppb, Average of Pyrolysis Single jar, Pyrolysis Comp. and Ox. dig. Hot Plate.
X32-30	S-1	14.7
X32-31	T-2	24.1
X32-32	S-3	18.0
X32-33	R-2	10.2
X32-34	T-4	22.6
X32-35	S-5	35.9
X32-36	T-6	20.5

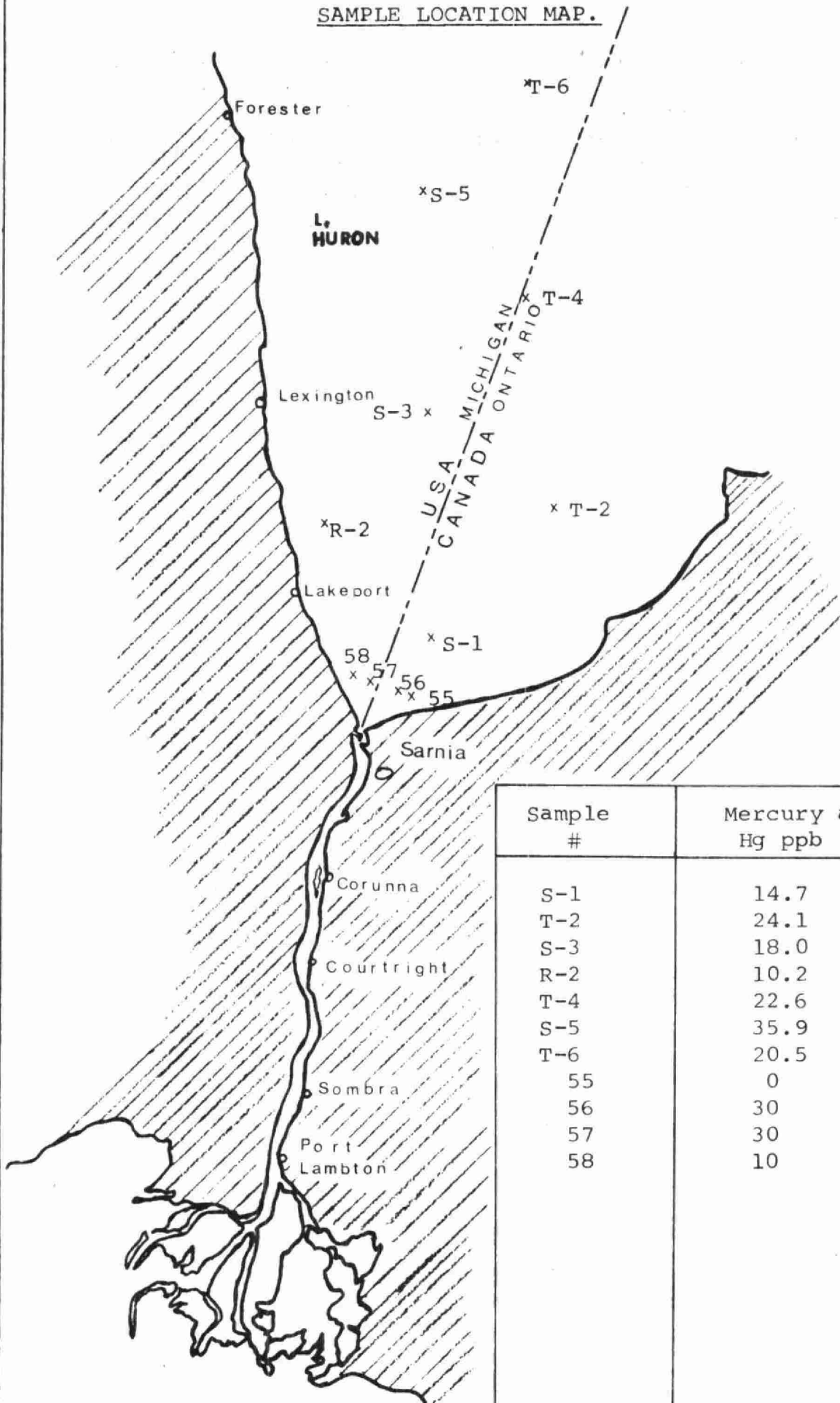
The stringent quality controls incorporated into the analytical procedures provided additional assurance regarding the validity of the data. Besides a series of round-robin sediments from the Environmental Protection Agency, in which we obtained data in excellent agreement with the mean values reported (14), there were numerous other controls tests performed.

An in-laboratory control sediment D1-A, was used to check the accuracy of the pyrolysis technique, the standard M.O.E. procedure and the water bath oxidizing digestion. The control sediment had been determined 52 times previously, establishing its mercury level. The following data was obtained from

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Fig. 1.

SAMPLE LOCATION MAP.



Sample #	Mercury as Hg ppb
S-1	14.7
T-2	24.1
S-3	18.0
R-2	10.2
T-4	22.6
S-5	35.9
T-6	20.5
55	0
56	30
57	30
58	10

duplicate analyses:

TABLE IV.

CONTROL DATA, SEDIMENTS.

Method	ppb Hg	% of Actual
Pyrolysis	2.3	97
M.O.E. Digestion.	2.4	100
Oxidation Digestion (Hot Plate)	2.6	108
Control Data	2.4 \pm 2%	-

Samples of the Lake Huron sediments were spiked with known amounts of methyl mercury chloride in aqueous solution, and pyrolysis and wet digestion analysis of these spikes yielded about 104% recovery of added mercury. Recoveries of mercuric chloride during this period ranged from 90 to 104%. This indicates that the methods employed do not lose mercury during preparation or analysis.

Precision on a control sediment was established as $\pm 2\%$ at the 2 ppm level for this period of time. This precision value indicates very good reproducibility in the preparation and analytical steps of the procedures employed.

Discussion.

The normal M.O.E. FAAS digestion (7) developed to analyze high levels of mercury in St. Clair sediments, was not sufficiently sensitive for the amount of sample taken. However, it did reveal that all of the stations sampled contained less than 50 ppb mercury. The pyrolysis method was the method of choice because of its reliability and excellent sensitivity. Using this technique, it appears that there is no need to composite the samples, since data from composite analyses were not demonstrably superior to those from single jar analyses.

Pyrolysis on dried composite samples was performed only in an attempt to ascertain the effects of drying, and this was done on four of the seven sediments with no conclusive data. It appears that losses during drying are dependent on the chemical composition and physical structure of the sediment. It is felt that future sediment studies should involve an estimation of the effects of drying on mercury content.

The oxidizing digestion in water bath (10) was performed in an attempt to provide data from a method different from the pyrolysis. However, the method, which is actually designed for water analysis, did not appear to be efficient enough to release all mercury from the sediment. In fact, in all but one sample the oxidation digestion in water bath yielded data significantly lower than the pyrolysis system.

Accordingly, an attempt was made to increase the oxidizing power of the EPA-KOPP water method by elevating the temperature to about 105°C on a hot plate. With this system, data was produced which tended to corroborate the pyrolysis data.

The data were not used to establish correlation numbers for each sample by different procedures because there was insufficient data and because sample heterogeneity, as indicated by the relative standard deviations (Table II) was quite high. The data shows, however, that the sediments from Lake Huron are in the range of 20 ppb, which is the same level established by the previous sets of analyses on Lake Huron sediments in the M.O.E. laboratory (6) (7).

The mean data for all sets of samples in the present experiment were averaged for each of the three most consistent analytical methods used, yielding 22 and 17 ppb for pyrolysis (single jar and composite jar, respectively) and 20 ppb by hot plate oxidation digestion. Thus, the mean of all data in this experiment is shown to be again around 20 ppb.

It is felt that methods of sample preparation which risk either loss of mercury or mercury contamination (drying, crushing, etc., at any temperature) or which significantly alter the mercury concentration in the portion of sediment used for the analysis (sieving or screening) should be avoided. This conclusion is substantiated by the in-laboratory checks performed by analyzing each sediment several times by three completely different procedures, all of which

indicated a fair degree of agreement, as seen in Table II.

Furthermore, in the complete absence of any data on the Lake Huron sediments that even approaches the lowest levels reported by C.C.I.W.-Barringer, the results reported by O.W.R.C./M.O.E. on these sediments should be considered to be the valid data.

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